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## Dissolved Constituents in Agricultural Drainage Waters


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# Dissolved Constituents in Agricultural Drainage Waters

## Abstract

Efflux of dissolved solutes in agricultural subsurface drainage systems adversely affects the ecosystems of receiving waters, degrades soil fertility, and represents an economic loss to farmers. These solutes are frequently studied without regard to their associated ions, which play a fundamental role in their transport characteristics. In this study, we conducted a literature review to identify major dissolved constituents in agricultural drainage waters characteristic of central Iowa and pinpointed causes of variability in the leaching rate of these constituents. This literature review is complemented by a thorough field investigation that analyzes major solute concentrations with respect to seasonal conditions, common cropping systems, and relationships among ions. Results from this investigation reveal that primary dissolved constituents consist of bicarbonate, calcium, nitrate, magnesium, chloride, sodium, and sulfate (in order of decreasing ppm concentration). Analysis of seasonal drainage samples showed that bicarbonate, calcium, and magnesium were present at greater concentrations during the post-growing season, while nitrate and chloride concentrations were greatest during the growing season. Seasonal variability of sulfate and sodium was negligible. Continuous corn and corn in annual rotation with soybeans had greater magnesium and chloride concentrations than soybeans in annual rotation with corn. Conversely, calcium concentrations were greater for soybean cropping systems compared to corn cropping systems. Bicarbonate and nitrate were not significantly different among any of the cropping systems. A strong correlation between bicarbonate and calcium suggests that agricultural lime dissolution was caused by mineral weathering, rather than by acidification due to N fertilizer applications or nitrification. An analysis of observed drainage flows, pH, and temperatures suggested that these parameters were not good indicators of differences in ionic composition.

## Keywords

Bicarbonate, Dissolved ions, Nitrate, pH, Subsurface drainage

## Disciplines

Agriculture | Bioresource and Agricultural Engineering | Water Resource Management

## Comments

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# DISSOLVED CONSTITUENTS IN AGRICULTURAL DRAINAGE WATERS

B. A. Zimmerman, A. L. Kaleita

**ABSTRACT.** *Efflux of dissolved solutes in agricultural subsurface drainage systems adversely affects the ecosystems of receiving waters, degrades soil fertility, and represents an economic loss to farmers. These solutes are frequently studied without regard to their associated ions, which play a fundamental role in their transport characteristics. In this study, we conducted a literature review to identify major dissolved constituents in agricultural drainage waters characteristic of central Iowa and pinpointed causes of variability in the leaching rate of these constituents. This literature review is complemented by a thorough field investigation that analyzes major solute concentrations with respect to seasonal conditions, common cropping systems, and relationships among ions. Results from this investigation reveal that primary dissolved constituents consist of bicarbonate, calcium, nitrate, magnesium, chloride, sodium, and sulfate (in order of decreasing ppm concentration). Analysis of seasonal drainage samples showed that bicarbonate, calcium, and magnesium were present at greater concentrations during the post-growing season, while nitrate and chloride concentrations were greatest during the growing season. Seasonal variability of sulfate and sodium was negligible. Continuous corn and corn in annual rotation with soybeans had greater magnesium and chloride concentrations than soybeans in annual rotation with corn. Conversely, calcium concentrations were greater for soybean cropping systems compared to corn cropping systems. Bicarbonate and nitrate were not significantly different among any of the cropping systems. A strong correlation between bicarbonate and calcium suggests that agricultural lime dissolution was caused by mineral weathering, rather than by acidification due to N fertilizer applications or nitrification. An analysis of observed drainage flows, pH, and temperatures suggested that these parameters were not good indicators of differences in ionic composition.*

**Keywords.** *Bicarbonate, Dissolved ions, Nitrate, pH, Subsurface drainage.*

**A**rtificial subsurface drainage is common in agricultural regions with high water tables and poorly drained soils (Helmert et al., 2005). Modern subsurface drainage systems consist of perforated pipe networks placed below the root zone, typically at a depth of 0.9 to 1.2 m from the soil surface, thereby providing a pathway for water to flow from the upper soil horizons. This drainage promotes crop growth and increases crop yield in poorly drained soils (Baker et al., 2004). As water drains through the soil profile, it dissolves parent minerals and electrolytes, causing them to dissociate into their component cations and anions (Bower, 1974; Rhoades et al., 1973). Drainage systems then convey these solutes from the subsoil to surface water bodies. Solute transported in this manner may represent an economic loss to farmers in the form of lost nutrients, may adversely affect downstream ecosystems, and can be expensive to remove from drinking water sources. These issues are illustrated most prominently with agricultural efflux of nitrate ( $\text{NO}_3^-$ ), which is responsible in large

part for the hypoxic zone in the Gulf of Mexico (Rabalais et al., 2001; Schilling and Libra, 2000). Nitrate efflux in Iowa drainage waters accounts for approximately 25% of the total nitrate that enters the Gulf of Mexico from the Mississippi River (Schilling and Libra, 2000). Other solutes, such as calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ), contribute to water hardness and soil acidity when they are leached from the soil, which increases drinking water treatment costs (Ravindra and Kaushik, 2003; Madramootoo et al., 1997) and land management costs by having to continuously apply agricultural lime. To develop effective mitigation strategies, it is beneficial to first understand what influences solute leaching rates and how solutes interact.

Land management practices and environmental conditions play a fundamental role in determining the rate of solute efflux from agricultural subsurface drainage. In the soil profile, electrolyte dissolution is a function of the percolation rate and groundwater flow path, both of which are influenced by the intensity and frequency of rainfall events, soil structure, soil type and geochemistry, tillage, cover, evapotranspiration, and cropping system (Bower, 1974; Daigh et al., 2014; Gribble, 2003; Liard et al., 2010; Thomas and Phillips, 1979; Trudgill et al., 1983; Stauffer and Rust, 1954). While the concentrations of leached ions are highly dependent on the characteristics of the percolating groundwater, they are also influenced by chemical ion-pair formations (Oster and McNeal, 1971), availability and solubility of exchangeable bases (Liard et al., 2010; MacIntire et al., 1952),

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soil pH (Kafkafi et al., 2001; White and Broadley, 2001; Zereini and Hötzel, 2008), ion affinity to the soil, and drainage water exposure to the atmosphere (Rhoades et al., 1973).

The relative abundance of an ion can also influence the leaching rate of other ions (Chao et al., 2011; Heng et al., 1991; Steele et al., 1984; Terman, 1977). The addition of  $\text{NH}_4^+$  or  $\text{Ca}^{2+}$  can displace  $\text{Na}^+$  and  $\text{Mg}^{2+}$  from soil exchange sites, as these ions ( $\text{Na}^+$  and  $\text{Mg}^{2+}$ ) have a lower affinity to the soil (Barber, 1995; Beckett, 1965; Poss and Saragoni, 1992), although  $\text{NH}_4^+$  is often rapidly converted to nitrate in humid environments where tile drainage is used. Dissolution of agricultural lime (calcite and dolomite) produces the dissociated ions  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{NO}_3^-$  (West and McBride, 2005). Baker et al. (1975) suggested that nitrate is toxic to sulfate-forming microorganisms, resulting in a negative relationship between  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations. These interactions have been demonstrated by the significant correlations among ions observed in the following studies. Steele et al. (1984) reported a strong linear correlation between the equivalent concentrations of  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  leached from a grazed pasture study site. Their study also found that  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  were both good predictors for estimating the concentrations of  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ . Correlation coefficients from the regression of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  on  $\text{NO}_3^-$  were 0.98, 0.90, 0.76, and 0.59 for fertilized plots and slightly lower for unfertilized plots. The positive correlation between  $\text{NO}_3^-$  and major cations observed by Steele et al. (1984) was also observed by Heng et al. (1991), where a near 1:1 relationship between total cation and anion molar concentrations was maintained in all drainage samples despite increases in N fertilization. A comprehensive review of ion leaching results from several published lysimeter studies was conducted by Terman (1977), whose conclusions further illustrate that the leaching rate characteristics of individual ions can be greatly influenced by the presence of other ions in the soil. It is important to note that not all the correlations observed in these studies were solely a result of ion interdependency. Processes such as drainage flow rate and crop uptake, as well as soil chemistry, could also have contributed to the strong correlations. Nonetheless, given our knowledge of ion-ion interactions, we can reasonably conclude that these correlations provide at least some evidence of ion-ion dependency.

As illustrated above, the leaching rate of individual ions is a function of several factors, including the presence of other ions. Complete knowledge of these processes and of the leaching response of major ions is essential for developing effective mitigation strategies. However, few published studies have conducted a comprehensive evaluation of the major dissolved constituents in agricultural drainage efflux, and even fewer have done so with real drainage samples (Heng et al., 1991). Furthermore, with increasing interest in developing dielectric sensors to monitor nitrate levels in such waters, it is important to have current data on the presence and dynamics of various ion species (e.g., Gali, 2014; Yunus and Mukhopadhyay, 2011). Therefore, in this study, we addressed this knowledge gap by first performing a literature review to identify the major dissolved constituents in agricultural subsurface drainage effluent with a focus on

Iowa drainage waters. Secondly, we complemented the literature review with a field investigation of major subsurface drainage water constituents. In so doing, we hope to (1) gain insight into ion-ion relationships; (2) evaluate compositional variability with respect to growing season and post-growing season drainage waters, as well as variability among three common cropping systems, drainage flow rate, pH, and temperature; and (3) quantify compositional differences between plot-scale and watershed-scale drainage waters.

## MATERIALS AND METHODS

Relevant research involving multiple ionic constituents in tile drain water, either as primary or secondary research objectives, was identified by searching the literature using Google Scholar, the Iowa State University Digital Repository, and Science Direct. A total of seven papers were identified, spanning the years 1974 to 2012. The number of studies we identified is relatively small, and many of them are fairly old. This raises questions about whether the findings are still relevant; however, given the small amount of published data on the ions present in tile drainage, other than nitrate, we elected to include them all. Drainage water constituents and their corresponding concentrations were synthesized from these published results for streams and drainage waters in regions with environmental conditions similar to those of central Iowa.

### FIELD INVESTIGATION

Water samples were collected and analyzed for major ion concentrations, as determined from the literature review, from subsurface drainage flow at two locations in central Iowa. A total of 44 samples were taken during the one-year study period from May to December 2015. Of the 44 samples, 40 were collected at the Iowa State University's Comparison of Biofuel Cropping System (COBS) research site and 4 samples were collected at the Hickory Grove watershed drainage district outlet. Both sites are described below. As part of parallel studies, it was important to collect samples from a variety of cropping systems, seasons, and locations. The sampling distribution was as follows: 4 samples from COBS at the end of May, 24 samples from COBS throughout June, 4 samples from both COBS and Hickory Grove throughout September and October, and 8 samples from COBS in mid-December. The primary collection site (COBS) consists of several hydraulically separated no-till research plots, which allow controlled experiments involving agricultural drainage water. By contrast, samples from Hickory Grove were of interest because they are representative of subsurface drainage effluent at the catchment scale from a typical Iowa watershed under intensive agricultural row cropping. The proximity of Hickory Grove to COBS (approximately 34 km NE of the COBS site) provided similar environmental conditions at both locations (i.e., precipitation, temperature, soil type, and leaching rate). Samples were collected during the post-growing season at Hickory Grove, as our interest in and access to this site was not realized until late in the study period.

## COBS STUDY AREA

The Iowa State University's Comparison of Biofuel Cropping System (COBS) research site is located in Boone County, Iowa (Liebman et al., 2007; Daigh et al., 2015). The COBS research site was established in 2008 and consists of 24 plots, each measuring 61 m long by 27 m wide, in a randomized complete block design with four replicates each of six cropping system treatments. Sampled cropping systems in this study are: corn on soybean rotation (C2), soybean on corn rotation (S2), continuous corn with stover removal (CC), and continuous unfertilized prairie (P). Soil distributions and properties were acquired from the USDA-NRCS Web Soil Survey (NRCS, 2016). The soil distribution is approximately 50% Webster clay loam at 0% to 2% slopes and 50% Nicollet loam at 1% to 3% slopes. The average soil texture distribution weighted over depth (0 to 2 m) is 41% sand, 38% silt, and 21% clay. Nicollet soils are classified as hydrologic soil group B, and Webster soils are in hydrologic soil group C. Nitrogen fertilizer was injected in the spring (prior to planting) as 32% urea ammonium nitrate (UAN) at a rate of 87 kg N ha<sup>-1</sup> on cropping systems C2 and CC. A second 32% UAN injection was performed in the spring after the corn emerged; application rates were 134 kg N ha<sup>-1</sup> on C2 plots and 112 kg N ha<sup>-1</sup> on CC plots. Agricultural lime was applied in the spring (prior to planting) at a rate of 13,050 kg ha<sup>-1</sup> (ECCE = 7,000 kg ha<sup>-1</sup>) on all corn and soybean plots (cropping systems = C2, S2, and CC).

Subsurface drainage is provided by 15 cm diameter corrugated plastic pipes placed at a depth of 1.1 m along the center line, lengthwise, of each plot. The plots are hydraulically separated by additional drainage lines placed between plots. Each center tile drains to a sump pit where cumulative flow is recorded with a mechanical flowmeter. A portion of the flow is collected in a 5 L container to provide flow-proportional water samples. For this study, 30 flow-weighted samples were used. Flow-weighted composite samples were acquired from an existing *in situ* flow-proportionate water collection system; flow was recorded from the flowmeter at the time of collection. An additional 12 samples were collected using grab sampling. Grab samples were collected during the post-growing season to maintain consistency with samples collected from Hickory Grove. Grab sampling was performed by collecting drainage water directly from the tile outlet. Flow for grab samples was determined by the time required to fill a 1 L sample container; time was recorded using a stopwatch.

## HICKORY GROVE STUDY AREA

The Hickory Grove Lake watershed is a subbasin of the South Skunk River basin (HUC ID: 07080105) in Story County, Iowa. Predominant soils in this region are poorly drained fine loam, fine silt, and coarse loam. Soil types consisting of Clarion, Nicollet, and Webster encompass 78% of the watershed. According to the Hickory Grove Lake Watershed Management Action Plan, approximately 74% of the watershed's soils are classified as hydrologic soil group B with hydraulic conductivities between 11 and 31 mm h<sup>-1</sup> (Andrews et al., n.d.). The watershed is 1633 ha in area and has median slopes of less than 2%. The prevailing land use

(84.7%) is row crops, with corn and soybean being the primary crops. The remaining land uses are grass (9.8%), forest (1.6%), water (2.2%), barren (0.9%), and artificial (0.7%) (IDNR, 2014). Gali et al. (2012) reported fertilizer applications of diammonium phosphate to soybean crops at a rate of 85 kg ha<sup>-1</sup> in the spring prior to planting, and anhydrous ammonia was applied to corn crops at a rate of 160 kg ha<sup>-1</sup> in the fall (after soybean harvest) and spring (prior to corn planting). Tillage consists of conservation, strip-till, and no-till practices (Gali et al., 2012), but the proportion and distribution of tillage practices is unknown.

A drainage district is located in the watershed's southeastern half and drains 879 ha of the 1633 ha area. The drainage district has a network of lateral drainage pipes that connect to the drainage district main line. The lateral pipes range from 12.7 to 25.4 cm in diameter and are placed at a depth of approximately 1.2 m. Twenty-three surface intakes are joined to the drainage network and only flow during rainfall-runoff events and ponding. All flow within the network is routed to the drainage district outlet, which is 91.44 cm in diameter. A small set ( $n = 4$ ) of grab samples was collected at the drainage district outlet during the post-growing season. Flow was determined by the depth of water from the pipe invert in conjunction with a rating curve developed by Gali et al. (2012). Data gathered at Hickory Grove were used to establish baseline conditions for watershed-scale drainage and compared to the mean drainage conditions observed across all samples at COBS.

## ANALYSIS OF FIELD SAMPLES

A Pocket Pro+ Multi 2 meter (Hach, Loveland, Colo.) was used to measure the pH and temperature of collected field samples. Based on the literature review (see the Results section), the following ions were identified for chemical analysis of the water samples from COBS: bicarbonate (HCO<sub>3</sub><sup>-</sup>), calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), chloride (Cl<sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and sodium (Na<sup>+</sup>). Chemical analyses were performed by the Iowa State Hygienic Laboratory (ISHL) in Ankeny, Iowa. Analysis methods used by ISHL are: EPA 300 for SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>; EPA 200.7 for Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>; LAC 10-107-06-IJ for NH<sub>3</sub>; and SM 2320B for alkalinity as CaCO<sub>3</sub> (reported as HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>). All ion concentrations were reported in ppm. Reported bicarbonate and nitrate concentrations were converted to mg HCO<sub>3</sub><sup>-</sup> L<sup>-1</sup> and mg NO<sub>3</sub><sup>-</sup> L<sup>-1</sup>, respectively.

Ions and electrolytes not included in the chemical analysis but present in the drainage water samples were assumed to be negligible, given their reported concentrations in the literature. This assumption was verified by evaluating the charge imbalance (CI) between the total cation and anion equivalent concentrations for each sample. Rhoades et al. (1973) and Heng et al. (1991) showed that the total equivalent concentration of cations in agricultural drainage waters tends to be in approximate balance with the total anions. This is illustrated more precisely in observations made by Steele et al. (1984) in which each unit increase in the equivalent concentration of NO<sub>3</sub><sup>-</sup> was balanced by an equal increase of cations (Ca<sup>2+</sup> > Mg<sup>2+</sup> > Na<sup>+</sup> > K<sup>+</sup> in order of increased equivalent concentration). Given these findings, it can be reason-

ably assumed that samples with significant CI values are either incomplete in their chemical analyses or contamination occurred during sample collection. The procedure used to calculate CI follows that identified by McCleskey et al. (2012), where CI is calculated using equation 1:

$$CI = \frac{(\Sigma cations - \Sigma anions)}{(\Sigma cations + \Sigma anions)/2} \quad (1)$$

where  $\Sigma cations$  and  $\Sigma anions$  are in the form of their milliequivalent concentration ( $\text{meq L}^{-1}$ ). A negative value for CI indicates that anions dominate the solution's overall charge, whereas a positive CI suggests that cations dominate. A commonly accepted value of  $CI > \pm 10\%$  is used as the criterion for eliminating samples with erroneous or incomplete chemical analysis.

Hypothesis testing was used to determine if there were significant differences in CI among groups: growing season versus post-growing season, by crop type, and by spatial aggregation level (plot-scale at COBS versus watershed-scale at Hickory Grove). Prior to hypothesis testing, the CI data were analyzed to determine normality and homogeneity of variance so that the appropriate hypothesis test could be selected. Groups under analysis were tested for both normality and homogeneity of variance using the Shapiro-Wilk test for normality and multi-group Levene test for homogeneity of variance. Results of these tests (not shown) suggested that the CI was normally distributed in all groups, and equal variance was confirmed for groups in comparison. Thus, a standard t-test was used for the two-group comparisons, and ANOVA was used for the cropping systems analysis, for determining any significant differences in CI. This testing and all statistical analyses in this study were done in Mathematica (Wolfram Research, Inc., Champaign, Ill.).

A small sample set ( $n = 4$ ) was collected from the Hickory Grove drainage district outlet for the purpose of quantifying differences in the ionic composition of watershed-scale drainage with plot-scale drainage from COBS. The proximity of Hickory Grove to COBS eliminates significant compositional differences caused by variations in climate and soil properties (soil properties at COBS and Hickory Grove are characteristic of the southern branch of the Des Moines Lobe). While the drainage system at COBS allows collection of flow-proportionate sampling, only grab samples were available at Hickory Grove. To ensure accurate comparisons between COBS and Hickory Grove, grab sampling was performed at COBS during the post-growing season, which correlates with the sampling period at Hickory Grove. Statistical comparisons between Hickory Grove and the COBS research site were limited, given that the drainage effluent at Hickory Grove is representative of several different cropping systems, tillage practices, and N fertilizer rates, whereas these parameters at COBS are precisely controlled. Therefore, the data gathered at Hickory Grove were used to establish baseline conditions for watershed-scale drainage and compared to the mean drainage conditions observed across all samples at COBS.

## PARAMETERS THAT INFLUENCE DRAINAGE COMPOSITION

Ikenberry et al. (2014) concluded that nitrate export was greatest during the early growing season and lowest in the post-growing season. Bower (1974) reported crop uptake as a significant sink of major ions; the magnitude of this uptake is significant enough to affect the ion leaching rate. Additionally, Terman (1977) concluded that the relative abundance of ions in the soil is the primary factor that determines ion leaching rates. In this study, we represented differences in these influential conditions with the following sampling groups: season (growing and post-growing) and cropping systems (C2, S2, and CC). Given different environmental conditions, crops, and N fertilization rates, we expected the drainage water compositions to be significantly different among these sampling groups. While differences in soil geochemistry may also affect the abundance of ions in the soil and the relative magnitude of ions present in tile drainage water, we did not consider soil geochemistry due to the relative similarity of the site morphology at COBS and between COBS and Hickory Grove.

From the literature review, we determined how the drainage composition was expected to change with respect to different seasonal conditions and different cropping systems. A statistical analysis was then carried out to determine if the collected field samples behaved accordingly. Analyses were performed on samples collected from the COBS research site; Hickory Grove samples were not included in these tests because there was no hydraulic separation between cropping systems and samples were not collected in both the growing and post-growing seasons. The Shapiro-Wilk test for normality indicated that the growing season and post-growing season ion concentration data were not normally distributed (results not shown). A Conover test was used to evaluate homogeneity of variance. Results (not shown) indicated sufficiently homogeneous variance between growing and post-growing season populations of  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^{2+}$ , and  $\text{SO}_4^{2-}$ , but homogeneity of variance was rejected at  $\alpha = 0.05$  for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The sampling distribution (fig. 3) of these ions ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) illustrates that the medians of the growing season and post-growing season sample distributions are not symmetrical about the interquartile range (IQR). It should be noted that hypothesis testing on  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was performed despite this departure from symmetry; therefore, test results alone may not be valid for these ions. Based on non-normal distribution but homogeneous variance, a Mann-Whitney test was used as a parametric alternative to ANOVA to test the null hypothesis for no differences in the median ranks of ion concentrations in growing season and post-growing season samples.

Within the growing season, observed concentrations (ppm) of  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^{2+}$ , and  $\text{SO}_4^{2-}$  were tested for normality and equality of variance prior to hypothesis testing. With the exception of  $\text{Cl}^-$ , the null hypothesis for normally distributed ion concentrations among all cropping systems was rejected according to the Shapiro-Wilk distribution. Therefore, rank-based non-parametric tests were performed to determine homogeneity of variance and equal median ion concentrations among cropping systems. Homogeneity of variance among cropping systems was confirmed for all ions according to the Conover test. The Kruskal-Wallis

test was used to test for identical ion population distributions (often referred to as a test for equal medians) among the three cropping systems. Midranks of ties were automatically calculated by Mathematica to accurately approximate the null distribution of the K-statistics by an appropriate chi-square distribution. Significant results against the null hypothesis were then subjected to an independent two-sample Mann-Whitney test for equal medians.

In addition to evaluating the effects of cropping system on drainage water composition, we also looked at the effects of cropping system on drainage flow volume, pH, and temperature. Significant differences in flow, pH, and temperature among cropping systems were tested to ascertain if these parameters corresponded with ionic composition. Dissimilar cropping system trends between these parameters and the ionic composition would suggest that these parameters cannot be used to make significant conclusions regarding ionic composition. Drainage flow volume, pH, and temperature all met the normality and variance assumptions for ANOVA (at  $\alpha = 0.05$ ); thus, we used this test to determine any difference among cropping systems.

### RELATIONSHIPS AMONG IONS

Heng et al. (1991), Steele et al. (1984), and Terman (1977) showed that there are significant relationships among major dissolved constituents. For example, Steele et al. (1984) found that the cumulative concentrations of major cations in drainage water responded proportionately to increased concentrations of nitrate. Furthermore, both Steele et al. (1984) and Terman (1977) observed significant linear correlations among most major solutes. In this study, we complement the work of Heng et al. (1991), Steele et al. (1984), and Terman (1977) by conducting a statistical analysis among ions to evaluate ion-ion relationships. Assumptions for normality and equality of variance were checked, and the results indicated that non-parametric tests were appropriate. Thus, rather than the linear regression analyses used in the previous studies, we used Kendall's tau rank correlation.

## RESULTS

Prior to conducting the field investigation, a review of the literature was performed, as described in the Methods sec-

tion, to identify the drainage water constituents that can be expected in field samples. Given the high costs associated with chemical analyses of sample analytes, these results were used to distinguish major constituents by their reported concentrations.

At least 12 dissociated ions can be present in central Iowa drainage waters (Bower, 1974; Gali et al., 2012) and streams (Barnes, 2001) (table 1). Note that an additional 18 electrolytes related to herbicides, pesticides, and personal care products are also known to be transported in agricultural drainage water in humid regions throughout the U.S. (table 1) (Gilliam et al., 1999; Gottschall et al., 2012; Muir and Baker, 1976). Assuming that all of these constituents would be present in samples from COBS and Hickory Grove, we expected an average total dissolved solids concentration of 508 ppm; this was calculated as the cumulative concentration of the 30 constituents identified in the literature. Primary dissolved constituents include the following free ions: bicarbonate ( $\text{HCO}_3^-$ ), calcium ( $\text{Ca}^{2+}$ ), nitrate ( $\text{NO}_3^-$ ), magnesium ( $\text{Mg}^{2+}$ ), sulfate ( $\text{SO}_4^{2-}$ ), chloride ( $\text{Cl}^-$ ), sodium ( $\text{Na}^+$ ), and sulfate ( $\text{SO}_4^{2-}$ ). The cumulative concentrations of reported  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  ions represent a substantial portion of all dissolved constituents ( $\approx 69.1\%$ );  $\text{NO}_3^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  account for approximately 29.7%; and the remaining minor constituents account for 1.2%.

In the following discussion, we describe the results from the literature review and the expected outcomes regarding ion concentrations with respect to different seasons and cropping systems.

Seasonal temperatures and precipitation are largely responsible for either the formation or immobilization of ions. When precipitation is sufficient to saturate the soils and temperatures are above  $10^\circ\text{C}$  (Gentry et al., 1998), anaerobic soil microbes may use nitrate ions as electron acceptors for respiration (Hoover, 2012). This process significantly reduces the leaching potential of nitrate and can represent as much as 33% of applied N fertilizer losses (Owens, 1960). Alternatively, nitrate's leaching potential is increased when aerobic soil microorganism oxidize residual nitrogen, in the form of ammonium ( $\text{NH}_4^+$ ), into the highly mobile form  $\text{NO}_3^-$ . This occurs when oxygen is readily available (i.e., lower saturation level) and soil temperatures are conducive. As with  $\text{NO}_3^-$ , the formation or immobilization of  $\text{SO}_4^{2-}$  is driven by microorganisms (e.g., Widdowson, 1970). Both nitrate and

**Table 1. Ionic constituents and associated concentrations reported in the literature for waters characteristic of agricultural subsurface drainage waters in central Iowa and similar humid regions throughout the U.S.**

Constituent	Conc. (ppm)	Location	Collection Period	Reference
$\text{HCO}_3^-$	252.60	Story and Carroll Counties, Iowa	April 1970 to May 1970	Bower (1974)
$\text{Ca}^{2+}$	98.20	Story and Carroll Counties, Iowa	April 1970 to May 1970	Bower (1974)
$\text{SO}_4^{2-}$	58.10	Boone, Carroll, and Story Counties, Iowa	April 1970 to Dec. 1972	Bower (1974) and Baker et al. (1975)
$\text{NO}_3^-$	36.65	Story County, Iowa	April 2011 to Oct. 2011	Gali et al. (2012)
$\text{Cl}^-$	25.20	Story and Carroll Counties, Iowa	April 1970 to May 1970	Bower (1974)
$\text{Mg}^{2+}$	24.30	Story and Carroll Counties, Iowa	April 1970 to May 1970	Bower (1974)
$\text{Na}^+$	6.70	Story and Carroll Counties, Iowa	April 1970 to May 1970	Bower (1974)
$\text{K}^+$	3.20	Des Moines Lobe, Iowa	March 1996 to Sept. 1998	Barnes (2001)
$\text{NH}_4^+$	1.29	Story County, Iowa	April 2011 to Oct. 2011	Gali et al. (2012)
$\text{Fe}^{2+}$	1.00	Des Moines Lobe, Iowa	March 1996 to Sept. 1998	Barnes (2001)
$\text{F}^-$	0.31	Des Moines Lobe, Iowa	March 1996 to Sept. 1998	Barnes (2001)
$\text{PO}_4^{3-}$	0.02	Boone County, Iowa	May 1970 to Dec. 1972	Baker et al. (1975)
Other	0.23	Humid regions of U.S. and Canada	Varies from 1973 to 2009	Gilliam et al. (1999), Gottschall et al. (2012), and Muir and Baker (1976)
Total	507.79			

sulfate are oxidized and immobilized by microorganisms under similar soil conditions; however, the leaching rates of these ions are not always positively correlated, as illustrated by Baker et al. (1975), who suggested that elevated levels of nitrate were toxic to sulfur-oxidizing bacteria.

Land management practices and seasonal changes responsible for the formation and increased leaching potential of nitrate can indirectly lead to greater losses of associated cations. Steele et al. (1984) observed that concentrations of leached  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$  responded proportionately to changes in  $\text{NO}_3^{-}$ . Edwards et al. (1998) noted that  $\text{SO}_4^{2-}$  also associates with these major cations in the soil. One explanation for the observations of Steele et al. (1984) is that nitric acid ( $\text{HNO}_3$ ), produced from  $\text{NH}_4^{+}$  oxidization, reacts with calcium carbonate ( $\text{CaCO}_3$ ) in agricultural lime, causing  $\text{CaCO}_3$  to dissociate into  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NO}_3^{-}$  (West and McBride, 2005). When  $\text{NH}_4^{+}$  is not being actively oxidized and  $\text{HNO}_3$  is not available,  $\text{CaCO}_3$  and natural carbonic minerals dissolve in the presence  $\text{H}_2\text{O}$  and gaseous or organic carbonate ( $\text{CO}_2$ ) to form  $\text{HCO}_3^{-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  (Aquilina et al., 2012). The resulting  $\text{HCO}_3^{-}$  either remains in the soil or is leached out with the drained water (West and McBride, 2005). Several studies show that  $\text{HCO}_3^{-}$  export is positively correlated with flow (Markewitz et al., 2001; Oh and Raymond, 2006; Raymond and Cole, 2003; Whisner, 2009).

Chloride is similar to  $\text{HCO}_3^{-}$  and  $\text{NO}_3^{-}$  in that it is tightly linked to local hydrologic conditions, given their low affinities to the soil (Kafkafi et al., 2001; White and Broadley, 2001; Zereini and Hötzl, 2008). However, the concentration of  $\text{Cl}^{-}$  in Iowa drainage waters is much lower than the concentrations of  $\text{HCO}_3^{-}$  and  $\text{NO}_3^{-}$  because most of the  $\text{Cl}^{-}$  in naturally occurring minerals has already been weathered away (Murray, 2004) and atmospheric deposition becomes negligible with increasing distance from the ocean (Gribble, 2003; Junge and Werby, 1958; Kafkafi et al., 2001). Anthropogenic sources of  $\text{Cl}^{-}$ , such as nitrification inhibitors and  $\text{Cl}^{-}$  fertilizers, can temporarily increase the leaching rate of  $\text{Cl}^{-}$  (MacIntire et al., 1952). Similar to  $\text{Cl}^{-}$ ,  $\text{Na}^{+}$  concentrations are also low as a result of few natural and anthropogenic

sources. Atmospheric deposition decreases with increasing distance from the ocean (Junge and Werby, 1958). Fertilizer applications as manure and sodium nitrate can cause immediate spikes in the concentration of  $\text{Na}^{+}$  leached (Laird et al., 2010). Both Laird et al. (2010) and Heng et al. (1991) observed that leaching quantities of  $\text{Na}^{+}$  and  $\text{Cl}^{-}$  were proportionate to their atmospheric and fertilizer inputs.

Given knowledge regarding how different parameters influence the leaching rates of ions, we expected the following:

1. Optimal conditions for nitrification during the early growing season will result in greater concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NO}_3^{-}$  and lower concentrations of  $\text{HCO}_3^{-}$  and  $\text{SO}_4^{2-}$  in growing season drainage compared to post-growing season drainage.
2. N fertilized cropping systems (C2 and CC) will have greater losses of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NO}_3^{-}$  than unfertilized systems (S2), while  $\text{HCO}_3^{-}$  and  $\text{SO}_4^{2-}$  losses will be greatest for S2 systems.
3. The absence of significant and variable sources for  $\text{Cl}^{-}$  and  $\text{Na}^{+}$  will result in consistent leaching rates among seasons and cropping systems.

### OBSERVED ION CONCENTRATIONS

The cumulative concentrations of observed ions ( $\text{HCO}_3^{-}$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^{-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^{-}$ ,  $\text{Na}^{+}$ , and  $\text{SO}_4^{2-}$ ) in drainage samples collected from COBS and Hickory Grove were greater than the cumulative concentrations of the same ions reported by Baker et al. (1975), Bower (1974), and Gali et al. (2012) (fig. 1). This difference is mostly due to differences in  $\text{HCO}_3^{-}$  and  $\text{SO}_4^{2-}$ . Mean observed  $\text{HCO}_3^{-}$  concentrations were 124 ppm greater in COBS samples and 165 ppm greater in Hickory Grove samples than the mean  $\text{HCO}_3^{-}$  concentration reported by Bower (1974). Conversely, Baker et al. (1975) and Bower (1974) reported substantially higher concentrations of sulfate than we observed at COBS and Hickory Grove ( $M = 11$  ppm).

The concentrations of  $\text{Ca}^{2+}$ ,  $\text{NO}_3^{-}$ , and  $\text{Mg}^{2+}$  reported in the literature generally agreed with those observed at COBS and Hickory Grove. Hickory Grove samples were slightly

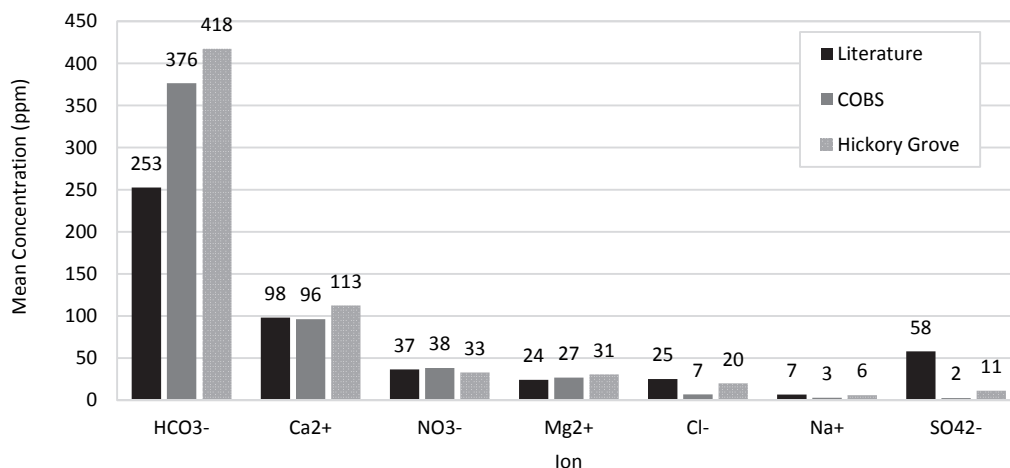


Figure 1. Mean ion concentrations reported in the literature (Baker et al., 1975; Bower, 1974; Gali et al., 2012) for primary dissolved constituents of agricultural drainage waters in Boone and Story Counties, Iowa, and mean ion concentrations observed in samples collected at the Iowa State University's Comparison of Biofuel Cropping System research site (Boone County, Iowa) and Hickory Grove Lake watershed drainage district outlet (Story County, Iowa).



greater in mean  $\text{Ca}^{2+}$  and lower in  $\text{NO}_3^-$  than the COBS samples and the literature values. However, as discussed in preceding sections of this article, the magnitude of this difference is likely attributable to environmental conditions. The mean  $\text{Cl}^-$  and  $\text{Na}^+$  contents in Hickory Grove samples were comparable to the literature values but substantially greater than the COBS samples (fig. 1).

The differences in sulfate concentrations could be attributed to stricter sulfur dioxide and sulfate aerosol emission standards for coal-burning power plants, which have dramatically reduced atmospheric sulfur deposition rates (Camberato et al., 2012). In fact, lower atmospheric inputs along with increased crop yields and a transition to low-sulfur fertilizers has led to an increasing number of sulfur deficiencies throughout the U.S. in recent years (Camberato et al., 2012; Eriksen et al., 2002; Sawyer and Barker, 2001; Schnug, 1998; Widdowson, 1970). This reduction in sulfate could have contributed to the greater concentrations of  $\text{HCO}_3^-$  to maintain a neutral charge balance between total cations and anions, especially considering that the primary cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) were approximately equal among the concentrations reported in the literature and observed at COBS and Hickory Grove.

Tillage was not specified by Baker et al. (1975); however, conventional tillage was reported by Bower (1974). Gali et al. (2012) reported varying tillage practices at the Hickory Grove sampling location, two of which were conservation and strip-till. Tillage can have a profound effect on the concentrations of ions leached from the soil, which may explain the higher  $\text{Cl}^-$  and  $\text{Na}^+$  concentrations reported by Bower (1974) and observed in Hickory Grove samples compared to those observed in COBS samples. Drainage water solute concentrations are greater when there is a displacement of the soil water in the main soil matrix rather than when there is rapid preferential movement of water through the soil profile (Trudgill et al., 1983). During high-intensity rainfall events, infiltrating water is conveyed primarily through macropores, resulting in rapid preferential movement of the water (Thomas and Phillips, 1979). When this occurs, there is little interaction with the soil matrix and therefore minimal diffusion of solutes from the smaller pores to the macropores (Thomas and Phillips, 1979). Preferential movement is reduced by conventional tillage in comparison to no-till practices (Kanwar et al., 1997). Tillage practices shear and close off macropores at the interface of the tilled and subsoil layers (Thomas and Phillips, 1979). Subsequently, tilled lands tend to have lower drainage flow volumes (Bakhsh et al., 2002; Randall and Iragavarapu, 1995) and higher solute concentrations (Weed and Kanwar, 1996).

#### CHARGE IMBALANCE CHECK

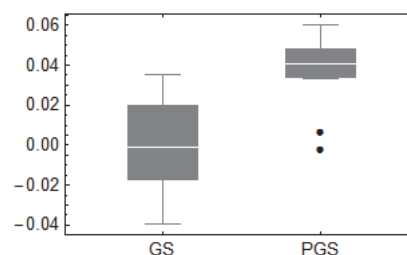
To verify that all major ions were captured in the chemical analysis of field samples, the charge imbalance (CI, eq. 1) was calculated for all samples collected in the field investigation. Of the 44 total samples, one sample had a  $\text{CI} > \pm 10\%$ . Per our established criterion, this sample was removed from further analysis. The distribution of the remaining calculated CI values favored cations but overall was centered close to zero ( $M = 1.4\%$ ,  $SD = 2.7\%$ ). This approximate neutral charge balance between total cations and total

anions coincides with observations of Heng et al. (1991), Rhoades et al. (1973), and Steele et al. (1984).

While CI was initially calculated as a quality control check, it became apparent upon reviewing the CI distribution that the slight positive skew was caused by COBS and Hickory Grove samples collected in September through December (fig. 2). The calculated CI was positive for all 4 samples from Hickory Grove and for 10 of the 11 COBS samples collected during this period. In contrast, 14 of the 28 COBS samples collected in May and June were positive (no samples were collected from Hickory Grove in May or June).

An independent-samples t-test indicated that CI was greater in COBS samples collected in September through December (post-growing season, PGS) than in COBS samples collected in May and June (growing season samples, GS),  $p$ -value (1-sided)  $< 0.001$  (table 2). This suggests that there may be another contributor to bulk electrical conductivity in the post-growing season that was not included in our chemical analysis, although a minor one since all the samples passed the CI threshold for quality. An independent-samples t-test suggested that the mean CI of COBS samples was not significantly different from that of Hickory Grove sample,  $p$ -value (2-sided)  $= 0.437$  (table 2). The final CI analysis evaluated the influence of cropping system on CI by comparing the mean CI of drainage from corn plots in annual rotation with soybeans (C2), soybean plots in annual rotation with corn (S2), and corn plots in continuous rotation (CC); the sampling distribution for each cropping system consisted only of samples collected during the growing season. An analysis of variance (ANOVA) showed that mean CI was not significantly different among cropping systems (C2, S2, and CC),  $p = 0.740$  (table 2).

Samples from prairie plots were not included in the CI analysis by season because prairie plots were not sampled during the post-growing season. Additionally, prairie plots are of little interest in the analysis of cropping system be-



**Figure 2.** Charge imbalance distribution for samples collected during the growing season (GS, May and June) and post-growing season (PGS, September through December) at the COBS research site in Boone County, Iowa.

**Table 2.** Distribution analysis of calculated charge imbalances (CI).

	GS	PGS	COBS	HG	C2	S2	CC
<i>n</i>	24	11	11	4	8	8	8
<i>M</i>	0.1%	3.6%	3.6%	2.8%	0.2%	-0.4%	0.4%
$\sigma^2$	0.05%	0.03%	0.03%	0.02%	0.05%	0.02%	0.08%
Student t-test and one-way ANOVA							
$H_0$	$\mu_{GS} \leq \mu_{PGS}$		$\mu_{COBS} = \mu_{HG}$		$\mu_{C2} = \mu_{CC} = \mu_{S2}$		
Var	$\sigma_p^2 = 0.0004$		$\sigma_p^2 = 0.0003$		$SS_B = 0.0003$ , $SS_W = 0.0108$		
DOF	$df_p = 33$		$df_p = 13$		$df_1 = 2$ , $df_2 = 21$		
Statistic	$t = -4.665$		$t = 0.802$		$F = 0.305$		
<i>p</i> -value	$<0.001$		0.437		0.740		

cause prairie crops are not commonly subject to artificial subsurface drainage in Iowa. However, we note that the mean CI of drainage from prairie plots ( $M = 3.6\%$ ,  $SD = 1.8\%$ ) was moderately greater than from C2, S2, and CC plots. The prairie CI distribution was skewed by one outlier, which was the second highest observed CI (6.77%) in all drainage samples. The remaining prairie samples had a negative mean CI of 0.1% and a standard deviation of 2.8%, which is more similar to that of the growing season samples from the C2, S2, and CC cropping systems. Given a larger sample size, it would be expected that the mean CI from prairie plots would trend toward neutral, similar to the other sampled cropping systems.

## PARAMETERS THAT INFLUENCE DRAINAGE COMPOSITION

### Seasonal Variability

Results from the CI analysis revealed that growing season samples were slightly but significantly different in composition from post-growing season samples. Here we identify the ions responsible for these seasonal differences with a statistical analysis of their observed concentrations. The mean total concentrations of observed ions in C2, S2, and CC samples increased from 534 ppm in the growing season to 575 ppm in the post-growing season. Specifically, the mean growing season concentrations of  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  increased by a cumulative 53 ppm in the post-growing season. Alternatively, the mean concentrations of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  decreased by a cumulative amount of 12 ppm. Ions with the most significant shift in concentration were  $\text{HCO}_3^-$  (increased by 40 ppm),  $\text{Ca}^{2+}$  (increased by 10 ppm), and  $\text{NO}_3^-$  (decreased by 8 ppm). The magnitude of change in  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  was minimal relative to that of  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{NO}_3^-$ .

Mann-Whitney test results for differences in ion concentrations were significant for  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$ . Based on the median ranks (table 3), observed ion distributions (fig. 3), and results from the Mann-Whitney tests, there is sufficient evidence to conclude that the median concentrations of  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were significantly lower in growing season samples compared to post-growing season samples. In contrast, the data suggest that the median concentrations of  $\text{NO}_3^-$  and  $\text{Cl}^-$  were greater in growing season samples. The null hypotheses for no difference in the median ranks of  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  were not rejected, indicating that  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  concentrations in the growing season and post-growing season samples were not significantly different.

The expected outcome of this analysis was that optimal conditions for nitrification during the early growing season would result in greater concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NO}_3^-$  and lower concentrations of  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  in growing season samples compared to post-growing season samples. Hypothesis testing on the ranked ion concentrations using the Mann-Whitney test provided supporting evidence for the expected outcome of higher  $\text{NO}_3^-$  and lower  $\text{HCO}_3^-$  concentrations during the growing season. Alternatively, test results provided sufficient evidence against our expected outcome for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , indicating that their concentrations were greater in post-growing season samples rather than in growing season samples. Accordingly, this suggests that dissolution of calcite and dolomite (primary sources of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions) was not caused by  $\text{HNO}_3$  (West and McBride, 2005), which is formed during nitrification. It was expected that no significant changes would occur in  $\text{Cl}^-$  and  $\text{Na}^+$ ; however, results indicated that chloride concentrations were greater during the growing season. This could be attributed to higher mineralization rates of residual organic chlorine during the growing season (Matchua et al., 2010). Sulfate concentrations were consistent among seasons, which is more characteristic of observations by Heng et al. (1991) rather than the inverse relationship with  $\text{NO}_3^-$  observed by Baker et al. (1975). Heng et al. (1991) attributed  $\text{SO}_4^{2-}$  stability to “ $\text{SO}_4^{2-}$  buffering in the soil solution, adsorption and desorption, and transformations to and from organic forms.”

### Variability among Cropping Systems

According to the Kruskal-Wallis test, the concentrations of  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  were not significantly different among cropping systems (table 4). However, the significance levels for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  provided sufficient evidence for significantly different ion concentrations in at least one sampling group (C2, S2, or CC) (table 4). An independent two-sample Mann-Whitney test on the median ranks of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{Na}^+$  provided insufficient evidence to suggest that these ions were significantly different between the C2 and CC cropping systems (table 5). Sulfate was significantly different among all cropping systems (table 5). Sodium concentrations in C2 were consistent with those of S2 and CC but significantly different between S2 and CC (table 5).

These results are inconsistent with what was expected based on the literature review. Bicarbonate concentrations were expected to be greatest in S2 cropping systems due to N fertilization in C2 and CC cropping systems. However,

**Table 3. Statistical analysis of different ion concentrations (ppm) in growing season (GS) and post-growing season (PGS) drainage water samples collected at the COBS research site.**

Test	Parameter	$\text{HCO}_3^-$	$\text{Ca}^{2+}$	$\text{NO}_3^-$	$\text{Mg}^{2+}$	$\text{Cl}^-$	$\text{Na}^+$	$\text{SO}_4^{2-}$
Growing season	$n = 24$							
	M	357	93	45	26	8	3	3
	$\sigma^2$	282	23	68	2	5	0	2
Post-growing season	$n = 11$							
	M	397	102	37	28	5	3	2
	$\sigma^2$	1319	70	109	5	2	0	0
Group ranks	GS: median, IQR	15.0, 16.6	14.5, 12.1	23.5, 12.1	14.5, 15.0	23.5, 13.9	13.8, 18.1	19.5, 17.0
	PGS: median, IQR	31.0, 14.3	27.5, 9.8	9.5, 8.5	29.0, 17.8	6.5, 10.8	23.0, 10.5	13.0, 16.3
Mann-Whitney	$H_0$ :	Growing and post-growing season parameters have the same distribution of scores (ranks)						
	U	49.5	46.5	209.0	49.0	234.5	103.0	167.5
	p-value	0.003	0.002	0.006	0.003	<0.001	0.292	0.213

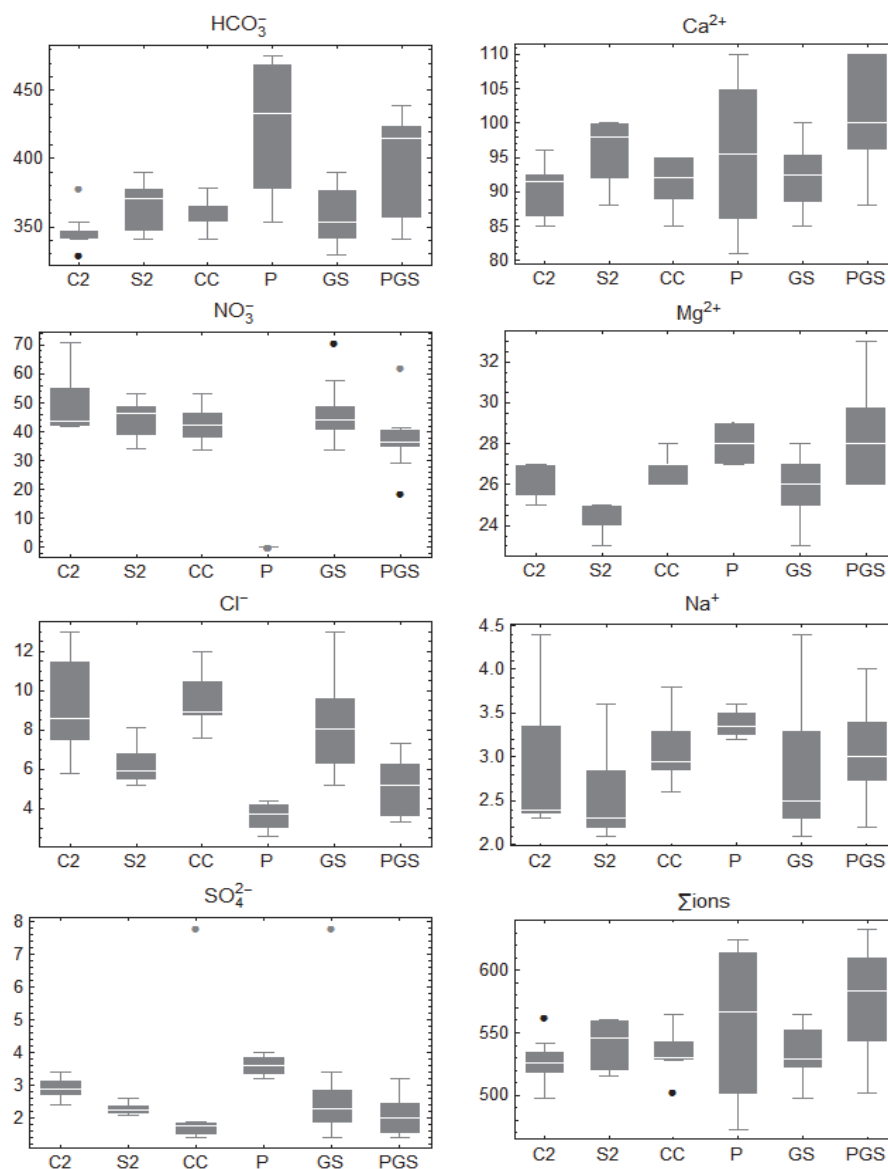


Figure 3. Distribution of observed ion concentrations (ppm) in drainage water samples collected at the COBS research site during the growing season (GS,  $n = 24$ ) and post-growing season (PGS,  $n = 11$ ). Distributions are also provided for growing season samples collected from different cropping systems: corn in annual rotation with soybeans (C2,  $n = 8$ ), soybeans in annual rotation with corn (S2,  $n = 8$ ), continuous corn crops (CC,  $n = 8$ ), and prairie crops (P,  $n = 4$ ).

Table 4. Statistical analysis for different ion concentrations (ppm) among growing and post-growing season drainage water samples collected at the COBS research site for cropping systems C2, S2, and CC.

Cropping System	Parameter	$\text{HCO}_3^-$	$\text{Ca}^{2+}$	$\text{NO}_3^-$	$\text{Mg}^{2+}$	$\text{Cl}^-$	$\text{Na}^+$	$\text{SO}_4^{2-}$
Corn in annual rotation with soybeans (C2)	$n = 8$							
	M	346	90	49	26	9	3	3
	$\sigma^2$	210	15	108	1	7	1	0
Soybeans in annual rotation with corn (S2)	$n = 8$							
	M	365	96	44	24	6	3	2
	$\sigma^2$	330	24	45	1	1	0	0
Corn in continuous annual rotation (CC)	$n = 8$							
	M	358	92	42	27	9	3	2
	$\sigma^2$	167	15	42	1	2	0	5
Kruskal-Wallis test		C2, S2, and CC are from identical populations						
	$H_0$ :							
	Statistic	5.565	6.140	1.922	15.260	11.992	6.218	13.031
	p-value	0.055	0.038	0.400	<0.001	<0.001	0.037	<0.001

both  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  had no significant differences among all cropping systems. Test results and ion distributions (fig. 3) indicate that  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  were significantly greater and  $\text{Ca}^{2+}$  was significantly lower in C2 and CC versus S2. Given com-

mon parent minerals for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, their leaching rates were expected to have a positive relationship. Perhaps  $\text{Mg}^{2+}$  replaced  $\text{Ca}^{2+}$  ions on the soil exchanges sites, leading to the negative relationship between these ions in S2 cropping systems.

**Table 5. Results of non-parametric Mann-Whitney distribution test for differences in ion concentrations among cropping systems.**

Parameter	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>
H <sub>0</sub> :	C2 and S2 are from identical populations				
U	11.0	61.0	57.0	49.0	61.5
p-value	0.023	0.002	0.010	0.076	0.002
H <sub>0</sub> :	C2 and CC are from identical populations				
U	26.5	26.5	28.5	16.0	56.0
p-value	0.525	0.483	0.674	0.080	0.013
H <sub>0</sub> :	S2 and CC are from identical populations				
U	50.5	0.0	1.0	13.5	56.0
p-value	0.056	<0.001	<0.001	0.045	0.013

### Drainage Flow Volume, pH, and Temperature

In the preceding analysis, it was determined that the ionic composition was significantly different among cropping systems. However, electrolyte dissolution and drainage composition are also dependent on the flow of water through the soil profile, soil water pH, and temperature (e.g., Bower, 1974; Kohnke et al., 1940; Stauffer and Rust, 1954; Thomas and Phillips, 1979; Trudgill et al., 1983). To determine if these parameters were in some way responsible for the different ionic compositions among cropping systems, observations of drainage water average daily flows, pH, and temperature were tested for significant differences among cropping systems.

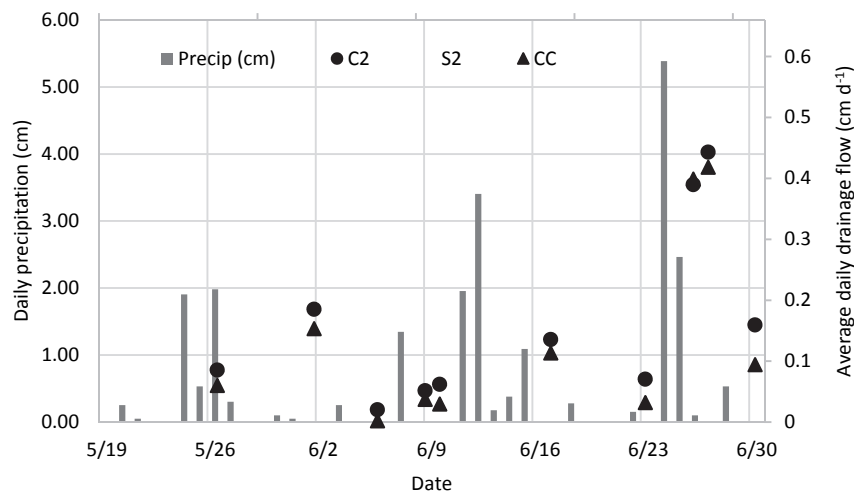
Bjorneberg et al. (1996) noted that NO<sub>3</sub><sup>-</sup> leaching rates were greatest early in the season. In mid-summer, evaporation rates often exceed precipitation, resulting infrequent drainage flows and lower ion losses. Considering that NO<sub>3</sub><sup>-</sup> is an ion with significant environmental relevance, drainage flow volumes were monitored in all plot replicates of each cropping system during the month of June to capture these high leaching rates. Drainage samples were collected between rainfall events and immediately following significant rainfall events. Flows ranged from 0.0002 to 0.590 cm d<sup>-1</sup>. Drainage flows during this sampling period responded proportionately to the depth of rainfall in all cropping systems (fig. 4). Flows tend to be strongly correlated with precipitation during the early growing season because the soil is saturated and evapotranspiration is generally lower than precipitation (Helmert et al., 2005). From May 19 to June 26, the cumulative precipitation was 22.71 cm; this precipitation pe-

riod corresponds to the cumulative flows observed from May 26 to June 30. Mean cumulative flow volumes from C2, S2, and CC were 6.97, 7.24, and 5.73 cm, respectively. Flow volumes among cropping systems were not significantly different according to the ANOVA F-test, F(2,37) = 0.726, p = 0.491. Because the flows were not significantly different among cropping systems, but ionic compositions were, we can therefore conclude that some other factor was responsible for the difference in ionic compositions.

Helling et al. (1964) observed a positive linear correlation between external pH and soil CEC. Thus, as pH increases, the total cation leaching potential decreases. Furthermore, drainage waters typically remain in equilibrium with respect to the equivalent total concentration of cations and anions (Heng et al., 1991; Rhoades et al., 1973). Therefore, it was assumed that as pH increases, the quantity of ions leached from the soil decreases. In addition, both pH and temperature are significant factors that determine the nitrification rate (Kamprath and Foy, 1985; Truog, 1947). A total of 42 drainage samples were analyzed for pH and temperature during four drainage events in June. Measurements were taken from four different plot replicates for each cropping system (C2, S2, and CC). The ANOVA results suggested no significant differences among C2, S2, CC cropping systems, F(2,39) = 0.726, p = 0.490. Similarly, no differences in temperature were observed among cropping systems, F(2,39) = 0.456, p = 0.637. Similar to our analysis of drainage flow, the lack of any differences in pH and temperature among cropping systems suggests that these parameters can be ruled out as significant contributors to the variability of ion leaching among cropping systems.

### RELATIONSHIPS AMONG IONS

Significant results for the Kendall tau rank correlation coefficient and corresponding significance for independence are presented here to establish the extent of ion-to-ion relationships in our samples. These results suggest that increases in HCO<sub>3</sub><sup>-</sup> are proportionate to Ca<sup>2+</sup> (τ = 0.645) (fig. 5). Additionally, as the concentration of HCO<sub>3</sub><sup>-</sup> increased, the concentrations of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> decreased (τ = -0.3460 and -0.425) (fig. 5). This agrees with the conclusions made from



**Figure 4. Observed growing season drainage from sampled plots at COBS and daily precipitation recorded by the AMES 8 WSW weather station located approximately 11.7 km (7.3 miles) north of the COBS research site.**

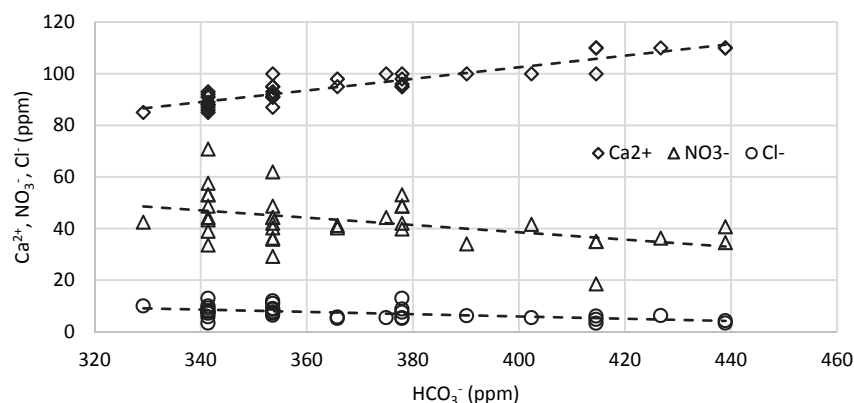


Figure 5. Significant correlations among ion concentrations observed in collected drainage water samples.

the seasonal analysis, where the concentrations of both  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  increased from the growing season to the post-growing season while  $\text{NO}_3^-$  and  $\text{Cl}^-$  decreased. However, these results do not agree with those of Heng et al. (1991), Steele et al. (1984), and Terman (1977), who observed a positive correlation between  $\text{NO}_3^-$  and major cations. No significant correlations were observed for  $\text{Na}^+$  or  $\text{SO}_4^{2-}$ .

## CONCLUSIONS

The data presented here represent only two sites within one region for a single season. As such, these data should not be interpreted as widely representative until similar data are reported for other sites and years. Nonetheless, this study provides information on a subject that is not well documented in the literature.

Primary dissolved ions in central Iowa agricultural drainage waters consist of  $\text{HCO}_3^- > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-}$  (in order of ppm concentration). These ions represent approximately 98.8% of all known dissolved constituents reported in published results for similar waters. We had expected the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NO}_3^-$  to be greatest during the early growing season when nitrification rates would be high. Similarly, we expected  $\text{HCO}_3^-$  to be low during the growing season due to a larger portion of agricultural lime dissolving into  $\text{CO}_2$  rather than  $\text{HCO}_3^-$ . However, the field investigation revealed that  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were present in the drainage water at greater concentrations during the post-growing season, whereas  $\text{NO}_3^-$  and  $\text{Cl}^-$  were greater during the growing season. Higher  $\text{Cl}^-$  concentrations during the growing season could have been due to increased mineralization rates. No seasonal differences were observed in  $\text{SO}_4^{2-}$  or  $\text{Na}^+$  concentrations. There was a significant positive correlation between  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$ , and a negative correlation between  $\text{HCO}_3^-$  and nitrate and chloride.

The ionic compositions of sampled drainage waters were also significantly influenced by cropping system. Magnesium and  $\text{Cl}^-$  were greater in C2 and CC than in S2. Calcium

and  $\text{Mg}^{2+}$  were expected to be greater in C2 and CC, given that these cropping systems were subject to external N fertilizer applications. However, the lack of any significant correlation between  $\text{NO}_3^-$  and  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  suggests that this reasoning is invalid. Assuming that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are derived from the same parent minerals, and that drainage waters tend to maintain neutral charge balances, we should expect either  $\text{NO}_3^-$  or  $\text{HCO}_3^-$  to be significantly different among cropping systems as well. Results from hypothesis testing suggested otherwise, as neither  $\text{NO}_3^-$  nor  $\text{HCO}_3^-$  were significantly different among cropping systems. It was also determined that neither drainage flow volume, drainage pH, nor drainage temperature were significantly different among cropping systems; this implies that these parameters cannot be used as descriptive variables for ionic composition.

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